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THE UNIVERSITY OF MINNESOTA

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TECHNICAL PROGRESS REPORT

FOR

DEPARTMENT OF ENERGY

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EXPERIMENTAL FORMATION OF CHALK FROM

CALCAREOUS OOZE

Starting Date: February 15, 1981

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INVESTIGATIONS TO DATE

Sample Collection and Procedures:

We collected 21 box cores of calcareous ooze in Fall, 1978, from the tropical and equatorial Atlantic, aboard the R/V Melville of Scripps Institution of Oceanography (Fig. 1). A suite of samples was recovered that exhibits a broad range of abundances of calcium carbonate, clay and biogenic opal (Table 1, Fig. 2). In addition the carbonate fraction includes varying abundances of low-magnesium calcite derived from forams and coccoliths, and aragonite derived from pteropods. The box cores were subsampled carefully within six hours after recovery to preserve the in-situ physical properties of the sediments as much as possible. Sufficient material was obtained for physical properties measurements and hydrothermal experimentation. The samples were capped, placed in a container of seawater, and stored in a refrigerator at 4°C aboard ship. The sediment subcores were transported to the University of Minnesota in seawater and have been stored in seawater at 4°C since they were collected. Consequently we have a suite of well-preserved samples of calcareous ooze that is ideally suited for experimental studies of diagenesis and the factors that influence it.

Enough sediment was collected from each core to allow measurements of several parameters on splits of the samples that were to be subjected to hydrothermal alteration. Measurement techniques were those used by Johnson et al. (1977). Bulk density and porosity were determined by standard mass-volume measurements. Percent calcium carbonate was determined from the volume of CO₂ evolved upon reaction of a known weight of sediment with a known volume of 37% HCl. Grain size distributions were determined from standard sieve and pipette techniques. Sediment texture, microfossil preservation, dissolution effects,

Figure 1. Locations of box cores taken on the Scripps Institution of Oceanography's Indomed Expedition. The 3 km and 4 km bathymetric contours are added to delineate the Mid-Atlantic Ridge.

Figure 2. Graph of water depth versus latitude for core sites.

- i) numbers refer to box core numbers
- ii) geometric shapes represent the following:
 - circles = calcareous ooze
 - triangles = marl
 - squares - pelagic clay
- iii) "R" indicates presence of radiolarians in the sample
- "P" indicates presence of pteropods in the sample

TABLE 1

Core locations and sediment composition. Cores denoted with an asterick (*) are tentatively selected for hydrothermal experiments.

Core	Lat.	Long.	Depth (m)	Sediment Type			Additional Pteropods	Components Radiolarian
				Clay	Marl	Ooze		
98*	16-56N	54-48W	5708	X				
94*	16-44N	51-32W	4391			X		
96	16-44N	49-24W	4588			X		
97*	16-39N	46-07W	3644			X	X	
98	15-30N	42-55W	4742			X		
100*	10-59N	34-09W	5393		X			X
101	6-57N	26-27W	4100			X		X
103	5-51N	24-27W	4492			X		X
104*	4-14N	21-56W	3331			X		X
106	2-41N	20-55W	4723			X		X
109*	5-31S	15-55W	3896			X		X
110*	10-05S	13-27W	1975			X	X	X
111*	12-40S	13-47W	3069			X	X	X
113*	15-16S	14-54W	3468			X	X	
115	17-38S	16-09W	3424			X	X	
116*	21-54S	18-42W	4718		X			
117	24-04S	19-57W	4398		X			
120	28-50S	31-18W	1937			X	X	
121*	28-57S	31-40W	3943			X		
122	29-17S	33-04W	3078			X	X	
129*	29-56S	34-35W	1479			X	X	

and overgrowth features were examined with a scanning electron microscope. The relative abundance of carbonate minerals were determined by x-ray diffraction, and the abundances of forams, coccoliths, pteropods, radiolarians and diatoms were estimated by optical microscopy. Clays were separated from the sediment by dissolving the carbonates in a sodium acetate-acetic acid solution at pH = 5, and their mineralogy was determined using x-ray diffraction. Permeability measurements will be made on subcores in future experiments using apparatus now under construction in our lab. We also hope to measure compressional sound velocity on altered sediments, since this will be a good means to indirectly assess extent of diagenetic modification.

Experimental Facilities:

The experimental apparatus employed for the first phase of this investigation was the same as that described by Dickson et al. (1963) and Sakai and Dickson (1978) with modifications described by Seyfried et al. (1979) (Fig. 3). This apparatus consists of a gold reaction cell (approximately 240 cc volume) held within a stainless steel pressure vessel which in turn is contained within its own furnace. A temperature controller maintains the furnace temperature generally at $\pm 1\%$ of the desired value. The gold reaction cell is pressure sealed to a detachable titanium top, which can be easily removed at the end of the experiment. A gold filter ($\sim 2 \mu$ porosity) at the bottom of the titanium top is connected directly to a gold capillary tube which terminates in a non-contaminated steel-jacketed Ti valve block external to the furnace. The system is pressured by pumping water into the void space within the pressure vessel surrounding the reaction cell.

An advantage of the Dickson type hydrothermal equipment is that sampling of

Figure 3. Schematic illustration of hydrothermal solution equipment and new gold-titanium reaction cell.

the aqueous phase can be carried out without disturbing the pressure and temperature of the experiment. When the sampling valve is opened, the reacted fluid is forced from the pressure vessel by the high hydrostatic pressure initially generated by the hydraulic pump. Solution samples can be withdrawn or fresh fluid added to the reaction cell at any time during the experiment. At the end of the experiment the pressure vessel can be quenched rapidly and alteration products effectively retrieved for analysis of physical properties, mineralogy and chemical composition.

Since carbonate diagenesis is profoundly affected by solution transfer with burial, it was desirable to simulate overburden through application of a lithostatic pressure onto the sediment. A sediment cannister was designed by Dr. George Shaw of the University of Minnesota, Department of Geology and Geophysics, that allows a uniaxial load to be placed on the sample at experimental conditions. A titanium cylinder contained the sample, while a titanium piston imparted a differential load (Fig. 4). The piston head was precisely machined to act as a sliding end piece for the cylinder; an attached piston rod was passed through the sediment into a sealed, air filled cavity at the base of the cannister. When loaded with sediment, the cannister was placed inside the gold plated pressure vessel, seawater added, and a hydrostatic pressure of 1000 bars added to the system. Since the hydrostatic pressure was not transmitted to the void space at the base of the piston, the piston head was pulled onto the sediment imparting a uniaxial pressure.

Sediment subcore that were subjected to hydrothermal alteration were transferred intact to the pressure vessel, thereby maintaining, as much as possible, the in-situ physical properties of the sediment. Future sediment samples will be in the form of cylinders, $1\frac{1}{4}$ " in diameter, 3" long, and enveloped in teflon

Figure 4. Titanium sediment container designed to impart a uniaxial load at experimental temperatures and hydrostatic pressures.

a) Schematic of container:

1. Titanium ring with drainage channels.
2. Titanium ring covering O-ring cavity.
3. Teflon O-ring.
4. Titanium cone which strengthens the O-ring seal.

b. Container under hydrostatic pressure. Uniaxial pressure is imparted to the sediment, since the cavity at the base of the piston rod remains at nearly atmospheric conditions.

jackets. A unique feature of our experimental design is that the original structure of the sediment is maintained and the sample is large enough to measure sound velocity and permeability on the final alteration product.

The sediment was subjected to temperatures of 275°C to 300°C for 30 days, at variable differential and hydrostatic pressures. Although a temperature of 300°C is much greater than that typically found in ooze-chalk sequences, reaction kinetics must be accelerated to generate significant lithification in a short period of time. Adelseck et al. (1973) found that significant precipitation of calcite occurs in nannofossil ooze within a month at 300°C but not at 200°C. The texture of their altered sediment closely resembled chalks recovered by the DSDP, which suggests that calcareous ooze diagenesis at abnormally high temperatures can produce a "normal" end product. Baker et al. (1980) found that significant calcite recrystallization can be obtained at lower temperature if the sediment is subjected to differential pressures of 800 bars at 130-175°C.

At the termination of an experiment the altered sediment was removed from the pressure vessel for analyses of bulk density, clay mineralogy and microtexture, as determined by optical and scanning electron microscopy. These results were compared to the same parameters for the unaltered sediment.

The rate and degree of lithification of each experiment was compared to the initial composition of the sediment to determine how these factors were affected by: 1) presence of aragonite (pteropods), 2) percent and preservation of calcite (forams and coccoliths), 3) approximate percent and mineralogy of clay, and 4) presence of biogenic opal (radiolarians and diatoms). The cores that provide the broadest range of composition were selected for the experimental study and are denoted by asterisks in Table 1. Separate runs were made on two subsamples from each core to estimate reproducibility of our results.

Solution Analyses:

Solution samples (approximately 10 ml) drawn into a gas-tight syringe were filtered through a 0.1 μm cellulose membrane and subdivided by weight. Labile components such as total dissolved H_2S ($\Sigma \text{H}_2\text{S}$), pH and total dissolved CO_2 (ΣCO_2) were analyzed immediately by selective ion electrode and total carbon analyser (Oceanography International), while a second aliquot was acidified with ultrapure HNO_3 and preserved for subsequent analysis by atomic absorption spectrophotometry and plasma source emission spectrometry. Chloride was determined potentiometrically and SO_4 was determined by ion chromatography. A third aliquot was diluted, separated and analyzed for dissolved SiO_2 by plasma emission. On 10 ml of solution we routinely analyze the following components: Na, Mg, Ca, K, SO_4 , SiO_2 , Cl, Sr, Fe, Mn, Ni, Zn, pH, H_2S , ΣCO_2 , and B. Uncertainties are $\pm 2\%$ for Na, Ca, K, SiO_2 and Cl; 8% for Mg at ≤ 10 ppm and 1% for > 10 ppm; 3% for B, Sr, and CO_2 ; 10% for Fe, Mn, Ni, and Zn; 15% for H_2S ; and 3% for SO_4 . The reported pH values are accurate to 0.05 pH units.

By monitoring solution chemistry we have a means of assessing reaction progress, and can obtain a better understanding of the mechanism by which lithification takes place. In future experiments we will integrate the measured concentrations of dissolved species with appropriate mass balance reactions and dissociational equilibria and, using the computer program 'SOLVEQ' (Reed, 1977; Seyfried and Dibble, 1979), calculate the distribution of aqueous species at the experimental temperature and pressure (e.g., 300°C and 500 bars). This will permit us to rigorously assess the degree of saturation of various carbonate minerals with respect to the aqueous phase. The recent compilation of internally consistent thermodynamic data for minerals, ions and gases by Helgeson et al. (1979) make this possible. At the end of the experiment we can then compare

the alteration mineral assemblage with that predicted by solution mineral equilibria.

RESULTS

Our experiments thus far have caused substantial changes in mineralogy, pore water chemistry, and microtextures of calcareous sediment. Although the major carbonate mineral in all the altered sediments remained low magnesium calcite, several transformations occurred in the noncarbonate fractions and are summarized in Figure 5. Relatively pure calcareous ooze displayed increases in both montmorillonite and albite abundance, while illite and kaolinite decreased. Less pure carbonates showed similar changes in clay mineralogy: montmorillonite again increased with concomitant decrease in illite and kaolinite. Unlike the carbonate-rich sediments, however, less albite was formed in the altered impure sediment.

Changes in solution chemistry reflected changes in relative abundances of clay minerals and formation of new phases (Fig. 5). For example, Mg concentrations in solution decreased during all experiments, a result of smectite formation. Correspondingly, solution pH decreased (see Bischoff and Seyfried, 1978), and calcite phases dissolved as evidenced by increased Ca concentrations in solution (Fig. 6). Smectite formation and H^+ generation was more apparent for clay-rich, calcareous ooze-seawater interaction than for pure calcareous ooze-seawater experiments (Fig. 7).

Significant differences in sediment microtextures resulted from the variable H^+ generated in the clay-rich and clay-poor sediments (Figs. 8-10). For example, the calcareous components in material where acid generation was important typically displayed very corroded surfaces, and little euhedral calcite was

Figure 5. Relative abundance of major noncarbonate minerals in impure carbonate oozes.

Figure 6. Change in aqueous species and pH during seawater-carbonate ooze interaction: ($\% \text{CaCO}_3 = 87$).

Figure 7. $[H^+]$ and aqueous species (ppm) versus % $CaCO_3$ for carbonate ooze-seawater interactions under differential pressure (after 72 hours).

Figure 8. Differential preservation of Gephyrocapsa oceanica, a solution-resistant coccolith: (a) Coccolith in altered clay-rich sediment (62% CaCO_3). The shield and central bar are corroded and not overgrown. (b) Shield in altered sediment of 98% calcium carbonate. The coccolith surface is less etched, and euhedral overgrowth is apparent both on inner cycle elements and on central crystals.

A

1 micrometer

B

1 micrometer

Figure 9. Calcareous ooze (98% CaCO_3) altered under differential pressure (30 days, 275°C , 1000 bars hydrostatic pressure). (a) Sturdy coccoliths in a matrix of abundant euhedral and subhedral coccoliths. (b) Extensively overgrown coccolith with proximal and distal shields cemented together.

A

2 micrometers

B

1 micrometer

Figure 10. Calcareous ooze (98% CaCO_3) altered under differential pressure (30 days, 275°C , 1000 bars hydrostatic pressure). (a) Coccolith cemented to foram surface. (b) Large matrix crystal which has physically incorporated smaller calcite particles and a whole nannofossil shield.

A

1 micrometer

B

1 micrometer

precipitated as overgrowths on individual nannofossil elements. In contrast, calcareous microfossils in the pure carbonates showed less evidence of surface etching while euhedral overgrowths were much more important both in number and size. The degree to which Mg-smectite formation affects carbonate diagenesis at burial depths encountered in typical marine chalks is not known. We need to determine if Mg-smectite forms at lower temperatures that are more representative of the real world, which we hope to do in the coming year. Additionally, the textural observations of our experiments could be tested by examination of smectite-rich and smectite-pore chalks and oozes recovered by the Deep Sea Drilling Project.

The greatest textural changes occurred in experiments where differential pressure was applied in addition to elevated temperature and hydrostatic pressure. Application of hydrostatic pressure alone resulted in dissolution and disaggregation of fragile nannofossils, a consequent increase in the abundance of individual matrix crystals, and occasional overgrowths on individual nannofossil elements. These are similar to the alterations observed in hydrothermal research by Adelseck et al. (1973). Addition of the relatively small differential pressure produced three other important changes in sediment texture (Figs. 9-10):

1. Increased nannofossil overgrowth.
2. Matrix crystal enlargement through secondary precipitation and incorporation of smaller calcite particles.
3. Cementation at grain boundaries resulting in welding of individual sedimentary components.

Since these are all traits observed with increasing burial depth in natural chalks, we expect that greater differential pressure in hydrothermal experiments

should reproduce even more accurately the modifications observed in carbonate sediments under substantial overburden. The experimental apparatus currently under construction in our lab will induce high differential pressures. We should achieve substantial diagenetic change in calcareous sediment at temperatures much lower (perhaps 100°-150°C) than the 275°C at which we had to conduct our previous experiments. Thus, we anticipate simulation of textural alterations encountered at temperature/pressure conditions more akin to those of burial depths in natural sediments.

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